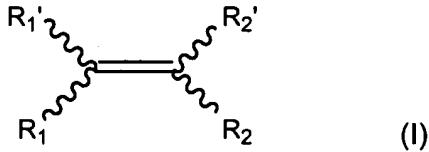


Claims

1. (original) A time temperature indicator for indicating a temperature change over time, comprising at least one indicator compound in a first isomeric form, which is converted into second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric or the second isomeric form of the indicator.
2. (original) The time-temperature indicator of claim 1, wherein the at least one indicator compound is a diarylethene or a spiroaromatic compound.
3. (currently amended) The time-temperature indicator [[of]] of claim 2, wherein the diarylethene is a compound of Formula (I)



wherein

R1 and R2 each independently represent C6-C14 aryl, C4-C12 heteroaryl, conjugated heterocyclic; wherein said heteroaryl and conjugated heterocyclic may contain one to three heteroatoms selected from N, O, [[or]] and S; and wherein said aryl, heteroaryl, or conjugated heterocyclic may be substituted by one or more halogen, hydroxyl, thiol, amino, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, -CH=CH-CN, azido, or amido;

R1' and R2' each independently represent H, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, or amido; or substituted or unsubstituted C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic; or R1' and R2' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring or a

C4-C7 heterocyclic ring containing one to three endocyclic or exocyclic heteroatoms selected from N, O, [[or]] and S; said N heteroatom may be further substituted by H, or by one or two substituted or unsubstituted groups selected from C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, [[or]] and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic [[or]] and inorganic anions, and optionally wherein said C5-C8 carbocycle is substituted by one or more halogen, preferably by one or more fluoro atoms; and optionally

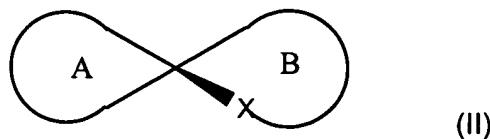
R1, R1', R2 and R2' each independently represent a charged group or a group substituted by another group having a charge; said charge may be localized or delocalized and may be positive or negative;

and wherein said R1 and R2 are in a cis or trans conformation.

4. (currently amended) The time-temperature indicator of claim 3, wherein the diarylethene is

- (a) a symmetric diarylethene, preferably selected from the group consisting of 1,2-dicyano-1,2-bis(2,4,5-trimethylthiophene-3-yl)ethane (1); 2,3-bis(2,4,5-trimethylthiophene-3-yl)maleic anhydride (2); 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene (3); and 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene (4); or
- (b) an asymmetric diarylethene, preferably selected from the group consisting of 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl) maleic anhydride (5); and 2-(methoxybenzo[b]thiophene-3-yl)-3-(1,2-dimethyl-3-indolyl) maleic anhydride (6).

5. (currently amended) The time-temperature indicator of claim 2, wherein the spiroaromatic compound is a compound of Formula (II):



wherein

ring A represents a C5-C8 carbocycle, C4-C7 heterocycle containing at least one heteroatom selected from N, O, [[or]] and S; said N heteroatom may be further substituted by one or two

groups selected from C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, [[or]] and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic or inorganic anions; said C5-C8 carbocycle or C4-C7 heterocycle may be substituted by one or more of the groups selected from halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, azido, amido [[or]] and amino;

ring B represents a substituted or unsubstituted heterocycle containing at least one heteroatom X, said X being selected from N, O, and S; wherein said N atom may be further substituted by one or two groups selected from C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, or -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic or inorganic anions;

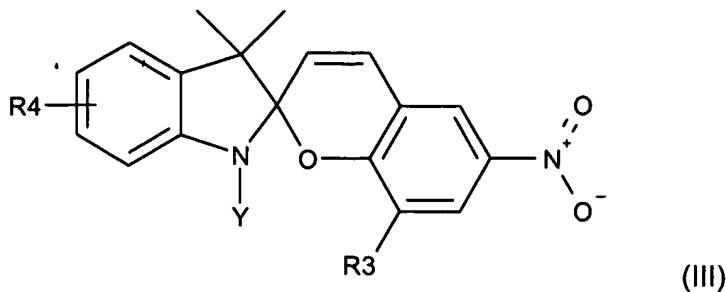
and wherein said ring B may contain one or more endocyclic double bonds and is optionally substituted by one or more halogen, ~~preferably by one or more fluoro atoms~~;

said rings A and B may be fused to one or more substituted or unsubstituted carbocycle, C4-C14 heterocycle, C6-C14 aryl or C4-C14 heteroaryl ring system;

and wherein the compounds of Formula II may be neutral, charged, multiply charged, positively charged having an external anion, negatively charged having an external cation or zwitterionic.

6. (currently amended) The time-temperature indicator of claim 5, wherein the spiroaromatic compound is a spiropyran derivative, ~~, preferably selected from the group consisting of 1',3',3',8-tetramethyl-5-hydroxymethyl-spiro(2H-pyran[2,3-c]pyridine-2,2'-2H-indole) and 1',3',3',8-tetramethyl-spiro(2H-pyran[2,3-c]pyridine-2,2'-2H-indole)~~.

7. (currently amended) The time-temperature indicator of claim 5, wherein the spiropyran derivative is a derivative of 1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-2H-indole) of Formula (III):



wherein

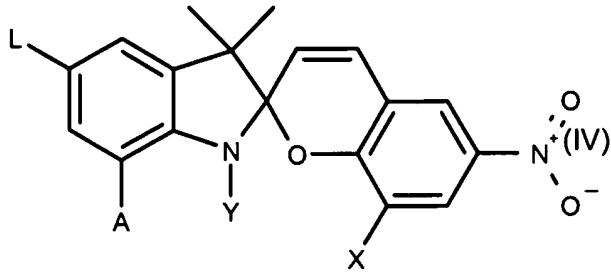
R3 is selected from the group consisting of H, halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, [[or]] and azido; wherein said alkyl, alkenyl, alkynyl, aryl, heteroaryl, and non-aromatic carbocycle may be substituted by one or more group selected from halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, [[or]] and sulfo;

R4 is selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl [[or]] and -CH=CH-CN; and

Y is selected from the group consisting of C1-C25 alkyl, ~~preferably methyl, n-propyl and n-octadecyl~~, and C7-C15 aralkyl, wherein said alkyl and aralkyl ~~may be~~ is optionally substituted by one or more group selected from halogen, ~~preferably fluorine~~.

8. (currently amended) The time-temperature indicator of [[C]] claim 5, wherein the spiroaromatic compounds include at least one of the following: spirooxazine or its derivatives, spironaphthoxazine or its derivatives, and spiroindolinopyridobenzoxazine or its derivatives.

9. (currently amended) A spiroaromatic compound of general Formula (IV):



wherein

A and L are independently of each other selected from the group consisting of H, halogen, C2-

C12 alkenyl, C2-C12 alkynyl and $\text{C}\equiv\text{R}$, wherein R is C1-C6 alkyl, C1-C6 alkoxy, C6-C14 aryl

and C7-C15 aralkyl; wherein said alkenyl, alkynyl and $\text{C}\equiv\text{R}$ may be substituted by one or more group selected from halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, sulfo, aryl and heteroaryl;

Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl ~~may be~~ is optionally substituted by one or more group selected from halogen, ~~preferably~~ fluorine; and

X is C1-C6 alkoxy or L;

with the proviso that Y is not n-propyl when L, A and X are hydrogen.

10. (original) The spiroaromatic compound of claim 9, wherein

L is hydrogen, Cl, Br or I;

Y is methyl, n-propyl, n-octadecyl or $\text{F}-\text{C}_6\text{H}_4-\text{C}_2\text{H}_5-$;

X is hydrogen or methoxy; and

A is hydrogen;

with the proviso that Y is not n-propyl when L and X are hydrogen.

11. (currently amended) A printing ink or printing ink concentrate, comprising the spiroaromatic compound of claim 9, ~~or~~ 10.

12. (currently amended) A high molecular weight material, comprising the spiroaromatic compound of claim 9, ~~or~~ 10.

13. (currently amended) A method of manufacturing a time-temperature indicator of claim 1 any of claims 1 to 8 comprising the steps of
- embedding in or atop a matrix said at least one indicator compound; and
 - inducing the formation of a metastable state of said embedded at least one indicator compound.
14. (currently amended) The method of claim 13 [[9]], further comprising the step of covering the time-temperature indicator with a cover support, ~~preferably designed to avoid photo recharging and/or photo bleaching~~.
15. (new) The time-temperature indicator of claim 6, wherein the spiropyran derivative is selected from the group consisting of 1',3',3',8-tetramethyl-5-hydroxymethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole) and 1',3',3',8-tetramethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole).
16. (new) The time-temperature indicator of claim 7, wherein in Formula (III) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.
17. (new) A spiroaromatic compound of claim 9, wherein in Formula (IV) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.
18. (new) A printing ink or printing ink concentrate, comprising the spiroaromatic compound of claim 10.
19. (new) A high molecular weight material, comprising the spiroaromatic compound of claim 10.
20. (new) The method of claim 14, wherein the cover support is designed to avoid photo recharging and/or photo bleaching.